

# Minerals In Salt Efflorescence and Leaching Of Metals in Mined Soils in SE Spain – Preliminary Results

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## 1. Abstract

Past mining activities in southeast Spain left a legacy of derelict landscapes devoid of vegetation and seasonal formation of salt efflorescence. Soils in these landscapes contain high amounts of Fe-oxyhydroxides, sulphates, and potentially leachable toxic metals (e.g., 27,515 mg Pb kg<sup>-1</sup>) due to extreme acidic conditions. The objective of the study is to characterize the minerals in salts efflorescence and the potential release of metals from mined soil in response to soil acidification. Based on color (e.g., pale yellow-10YR 8/2, pale brown-5Y 8/4, and red brown-5YR 5/3), we collected salt samples from several areas of evaporite accumulations. We used X-ray diffraction and electron microscopy to determine the mineral composition. We also excavated an undisturbed soil column (15-cm diameter and 30-cm length) from a representative site to elucidate the release of heavy metals from soils. The column was leached weekly with distilled water for 10 times to simulate rainfall events in the study areas. Leachates were collected and analyzed for various chemical properties. Results showed that salts were dominated by hydrated sulfate minerals of aluminum, iron, magnesium, manganese and zinc (or halotrichites). Apjohnite (MnAl<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>·22H<sub>2</sub>O) was observed in all samples although wupatkiite [(Co,Mg,Ni)Al<sub>2</sub>(SO<sub>4</sub>)<sub>4</sub>·22H<sub>2</sub>O] may also be present; apjohnite and wupatkiite had similar X-ray diffraction patterns. Our results supported earlier literature that halotrichites are common in areas where sulfur oxidation takes place. Leachates after week 1 had pH 2.2 and the highest soluble salt contents. The relative amounts of metals in the leachates followed the order Zn>>Cd>Cu>Pb and were interpreted to be strongly associated with the oxidation of sulphide minerals. These initial results were used to design a leaching experiment to evaluate the effectiveness of different soil amendments (e.g., pig manure and wastes from marble industry) to minimize the risk of metal release into the soil and groundwater.

## 2. Introduction

Mine tailings in the Sierra de Cartagena (SE Spain) are commonly stored in terraced silt ponds (or *balsas*). *Balsas* pose environmental hazards because they are known to collapse from excessive water erosion and/or seismic disturbances (e.g., Conesa et al., 2007). Problem soils dominate these *balsas* because of extreme acidity, high salinity and contain elevated contents of metals such as iron (Fe) cobalt (Co), copper (Cu), lead (Pb), magnesium (Mg) and zinc (Zn). Successful re-vegetation of mine wastes is proven to be one of the best reclamation techniques for mine tailings available to date (e.g., Norland and Veith, 1995; Freitas et al., 2004). However, the establishment of vegetation to stabilize *balsas* has many challenges including the removal of elevated levels of metals and high salinity (Ottenhoff et al., 2007; Tordoff et al., 2000). In the Sierra de Cartagena, high summer evaporation rates seasonally accumulate salts on soil surface creating a very hostile environment for plant growth. There is a need to understand the nature of salt efflorescence to effectively reclaim the problematic soils in *balsas* for effective and long-term establishment of vegetation.

The objectives of this paper are to (1) characterize the mineral composition, and (2) quantify the removal of salts through leaching in order to understand the nature of low acidity and high salt contents common in problem soils found in mine waste storage areas in the Sierra de Cartagena (Spain).

## 3. Materials and methods

### *Sample collection*

Soil samples were collected from the mined areas in the Sierra de Cartagena, southeast Spain. Surface soils were collected from the 0-10 cm depth while subsurface soils were taken at 30-cm depth. Salt samples were collected from eight main areas of salt accumulations. Each salt sample was ~ 1.0 kg and we used Munsell Soil Color Chart to describe the color of each salt sample. The salt minerals were group into three classes based on color: RB (Red Brown, 5-7.5 YR), PY (Pale Yellow, 2.5-5Y) and PB (Pale Brown, 10YR).

### *Leaching experiment*

This experiment is based on the studies Ashworth and Alloway (2004), Doye and Duchesne (2003), Camobreco et al., (1996), and recommended by ISO/DIS 18772 (2006). The undisturbed soil columns, ~ 35 cm thick, were extracted from a representative adjacent to a silt pond using methacrylate tubes (60 cm long and 15

cm inside diameter). Leaching were carried out for 11 weeks using 1,000 mL (50 L m<sup>-2</sup>) distilled water at a rate 8 mL min<sup>-1</sup>. Water applied corresponded to mean annual precipitation in Murcia Province (320 mm/yr). Leachates were analyzed for pH, EC and contents of Cu, Cd, Pb and Zn.

#### Chemical and mineralogical analyses

We determined the routine physical and chemical properties of the soil and salt samples using standard and conventional techniques (Bower and Wilcox, 1965; Peech, 1965; Risser and Baker, 1990; Buurman et al., 1996). These properties were soil pH, redox potential (Eh), electrical conductivity (EC), total and water-soluble contents of selected metals in soil and salt samples. We used atomic absorption spectrometer to measure cadmium (Cd), copper (Cu), lead (Pb) and zinc (Zn), and inductively coupled plasma mass spectrometer for iron (Fe), manganese (Mn), aluminium (Al), cobalt (Co) and nickel (Ni). Potassium (K), sodium (Na), magnesium (Mg), calcium (Ca), sulfate (SO<sub>4</sub><sup>2-</sup>) and chloride (Cl<sup>-</sup>) contents in soil solution were measured using ion chromatography.

The mineral composition of soils and salts were determined using X-ray diffraction (XRD) and scanning electron microcopy (SEM) techniques. We used a Bruker D8 X-ray diffractometer and mineral identification and semi-quantitative contents of minerals were determined by matching XRD pattern with the JCPDF Powder Diffraction Database 2 using EVA<sup>TM</sup> software. A Philips XLS 30 SEM equipped with EDAX<sup>TM</sup> energy dispersive system and a Be window was used in microscopic investigation.

## 4. Results

#### Chemical composition

The pH, EC, Eh and chemical composition of 1:5 salt:water extracts were summarized in Table 1. Low acidity in all salt samples was evident in pH 3.0 in PB group to pH 2.3 in PY minerals. The EC (dS m<sup>-1</sup>) ranged from 27 to 36 while Eh (mV) varied from 389 to 469. Among RB minerals, soluble aluminum (Al) was the dominant cations (57,575 mg Al kg<sup>-1</sup> salt) while soluble iron (133,303 mg Fe kg<sup>-1</sup> salt) and zinc (70,029 mg Zn kg<sup>-1</sup> salt) were the major cations in PY and PB groups, respectively. Other major cations with concentrations ~10<sup>3</sup> mg kg<sup>-1</sup> salt in the soil extracts were magnesium (Mg) and manganese (Mn). Metals observed in minor amounts (~10<sup>0</sup> to 10<sup>2</sup> mg kg<sup>-1</sup> salt) were cadmium (Cd), calcium (Ca), cobalt (Co), copper (Cu), lead (Pb), nickel (Ni), potassium (K) and sodium (Na). Sulfate and chloride dominated the anions in the solution extracts at ~ 1:4 SO<sub>4</sub><sup>2-</sup>:Cl<sup>-</sup> ratio.

**Table 1 pH, EC, Eh and mean (and standard error) soluble elements in various salt mineral groupings in silt ponds in the Sierra de Cartagena (Spain)**

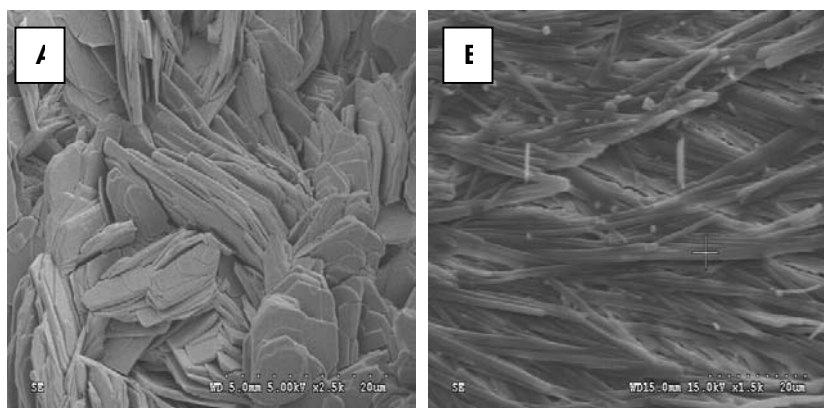
	Red Brown (n=2)	Pale Yellow (n=2)	Pale Brown (n=4)
pH 1:1 water	2.6 (0.10)	2.3 (0.79)	3.0 (0.13)
EC 1:5, dS m <sup>-1</sup>	30 (0.15)	27 (7.1)	36 (0.5)
Eh, mV	447 (32)	469 (56)	389 (16)
<i>Soluble cations (mg kg<sup>-1</sup> salt)</i>			
Aluminum	57575 (3484)	23930 (17350)	31865 (5204)
Cadmium	124 (37)	140 (111)	220 (30)
Calcium	5.4 (0.01)	17.2 (13.1)	21.0 (13.0)
Cobalt	26.4 (7.44)	27.6 (6.58)	38.3 (1.58)
Copper	310 (106)	1604 (422)	510 (138)
Iron	14818 (2491)	133303 (132379)	6028 (2929)
Lead	1.8 (0.17)	75.5 (73)	2.3 (0.15)
Magnesium	2119 (1123)	29768 (6315)	28799 (2308)
Manganese	11352 (2584)	10738 (10047)	23187 (4533)
Nickel	19.2 (16.9)	13.5 (13.5)	34.2 (10.9)
Potassium	2.1 (1.9)	88.1 (74.1)	44.5 (19.5)
Sodium	5.6 (3.4)	25 (22)	252 (144)
Zinc	34570 (1350)	30151 (20942)	70029 (10086)
<i>Soluble anions (mg kg<sup>-1</sup> salt)</i>			
Sulfate	443712 (25653)	449059 (5569)	495853 (13825)
Chloride	17105 (3909)	10779 (1539)	19727 (5511)

*n* = number of observations in the group; Red Brown (RB) = 5-7.5 YR; Pale Yellow (PY) = 2.5-5Y; Pale Brown (PB) = 10YR in Munsell notation

Surface and sub-surface soils collected in the study areas contained high contents of Pb and Zn. Soils where the PY group was observed had the highest Pb (11,190 mg Pb kg<sup>-1</sup> soil) and Zn (5,098 mg Zn kg<sup>-1</sup> soil) in both 0-10 cm and 30-cm layers. These amounts exceeded the Canadian Soil Quality Guidelines (Health Canada 2002). The contents of Cd, Cu, Pb and Zn in surface and sub-surface soils where RB group of halotricites precipitated were the lowest.

### Mineral composition

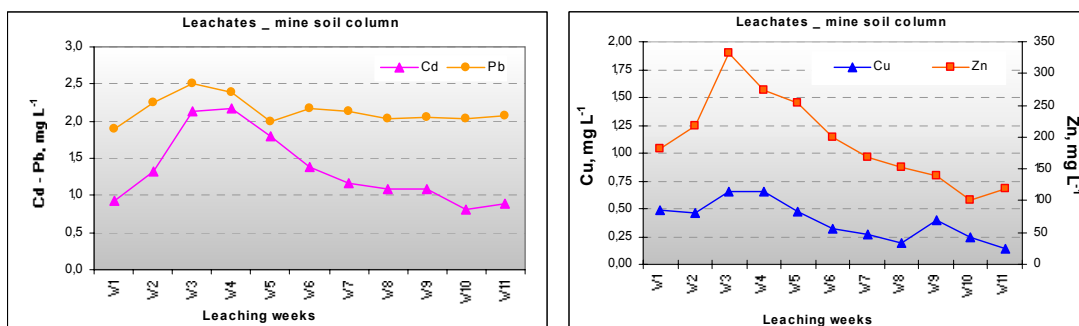
The salt efflorescence in silt ponds at the Sierra de Cartagena was dominated by sulfate minerals. These halotricities were composed of apjohnite ( $\text{MnAl}_2(\text{SO}_4)_4(\text{H}_2\text{O})_{22}$ ), copiapite ( $\text{Fe}_{0.69}\text{Fe}_4(\text{SO}_4)_6(\text{OH})_2(\text{H}_2\text{O})_{20}$ ), zinc sulphate hydrate ( $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$ ) and sulfates of magnesium such as starkeyite ( $\text{MgSO}_4 \cdot 4\text{H}_2\text{O}$ ), hexahydrate ( $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ ), and epsomite ( $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ ) (Fig. 1). Apjohnite and zinc sulphate hydrate were observed in each color groups while copiapite and epsomite were identified only in the PY and PB groups, respectively. Sample 44-1 (PY Group) was a monomineralic copiapite salt mineral. There were no chloride minerals identified in salt and soil samples collected in the study areas.



**Figure 1** Scanning electron micrographs of (A) copiapite [ $\text{Fe}_{0.69}\text{Fe}_4(\text{SO}_4)_6(\text{OH})_2(\text{H}_2\text{O})_{20}$ ], (B) apjohnite [ $\text{MnAl}_2(\text{SO}_4)_4(\text{H}_2\text{O})_{22}$ ] minerals collected from the Sierra de Cartagena (Spain)

### Leachate composition

Weekly leachates collected for 11 weeks showed that the highest EC ( $11.15 \text{ dS m}^{-1}$ ) corresponded to lowest pH (3.2) and highest concentrations of Cd, Cu, Pb, Zn, and sulfates. pH of leachate fluctuated  $\sim 3.6$  while Fe and sulfates contents showed maxima at  $21.3 \text{ mg L}^{-1}$  and  $8,270 \text{ mg L}^{-1}$ , respectively (data not shown). Metal contents in the leachates seemed to stabilize after 7 weeks for Cd, Cu and Pb and after 11 weeks for Zn (Fig. 2). We observed highest contents ( $\text{mg L}^{-1}$ ) of metals in leachates at week 3 and they were as follows: Zn - 331.4, Pb - 2.5, Cd - 2.13, and Cu - 0.65.



**Figure 2** Contents of Cd, Cu, Pb, and Zn in leachates collected from undisturbed soil column in Sierra de Cartagena (Spain)

## 5. Discussions

### Extreme acidity, salinity and salt accumulation

The oxidation of sulfidic waste rocks accumulated from  $>2,500$  years of metal extractions resulted to the extreme acidity and high salinity (mainly  $\text{SO}_4^{2-}$ ) in the study areas. Mined rocks in the Sierra de Cartagena consisted of iron ores such as iron oxides/hydroxides, sulfides, sulfates, carbonates and silicates; lead and zinc ores were galena, sphalerite, carbonates, sulfates and lead-and zinc-bearing oxides (Oen et al., 1975). The low pH in soils was due to the following reaction:  $\text{FeS}_2 + 7/2 \text{O}_2 + 3\text{H}_2\text{O} \rightarrow \text{Fe}^{3+} + 2\text{SO}_4^{2-} + 2\text{H}_3\text{O}^+ + \text{e}^-$ . The generation of  $\text{H}_3\text{O}^+$  in the reaction kept the pH of the soil low as well as mobilized metals. The high amount of soluble metals (e.g.,  $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ) and anions (e.g.,  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$ ) are responsible for the high EC in the soil. The low pH and high EC rendered the environment hostile to plants and organisms.

Oxidation of sulfide minerals generates high amounts of  $\text{SO}_4^{2-}$  in soil and when reacted with metals will form halotricities such as apjohnite and starkeyite. Based on the solubility products (ksp) of these salt minerals, the likely chronological sequence of formations followed apjohnite  $>$  copiapite  $>$  hexahydrate  $>$  zinc sulphate

hydrate > starkeyite. However, the relative amounts of metals (e.g., Mn, Al, Fe, Mg and Zn) will influence the actual precipitation of halotricites. Minerals where the *k<sub>sp</sub>* was exceeded first can be expected to precipitate earlier than undersaturated minerals.

#### *Metals in leachates*

The contents of Zn and Cd in leachates throughout the experiment exceeded the FAO guidelines for irrigation water (FAO, 1985) given at 0.01 and 2.0 mg L<sup>-1</sup>, respectively. However, Pb contents in leachates were never above the FAO guideline (5.0 mg Pb L<sup>-1</sup>) while Cu contents > FAO guideline (0.20 mg Cu L<sup>-1</sup>) in weeks 1 to 10 but decreased below the guideline after week 11.

The concentration of metals in leachates declined more rapidly for Zn and Cd than Cu and Pb which can indicate differential solubilities (or susceptibility to weathering) of minerals containing these metals. High content of Zn in first three weeks can be explained by the high solubility of halotricities such as zinc sulphate hydrate. The similarity in the behavior of Cd contents to those of Zn might indicate Cd-containing sulfate, however, none were detected perhaps due to quantity < detection limit of XRD technique (5%). Copper and Pb did not show high fluctuations perhaps due to non-existence of Cu- and Pb-containing sulfate minerals in the samples. The low pH (< 3.6) in leachates might also contribute to the mobilization of metals in the soil.

### **6. Conclusion and Implications to Management of Silt Ponds**

The minerals in salt efflorescence are dominated by halotricites mainly and might have been responsible for the elevated levels of Cd and Zn in leachates. The preliminary results suggest high acidity is the results of the oxidation of sulfide minerals in the tailing ponds. The high salinity, low pH and elevated levels of Zn, Pb, and other metals would prevent the establishment of plants. These initial results were useful in the design of leaching experiment to evaluate the effectiveness of different amendment techniques (e.g., use of industrial wastes such as pig manure and marble cuttings) to minimize the risk of metal release into the soil. A long-term laboratory leaching study would allow the understanding the effect of tailings on water contamination, thus contributing to the qualitative prediction of pollution on the basis of metal mobility.

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